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SPECTRAL SENSITIZATION OF DICHROMATED GELATIN (DCG) FOR AN IMPR--ETC(U)
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SPECTRAL SENSITIZATION OF DICHROMATED GELATIN (DCG)
FOR AN IMPROVED HOLOGRAPHIC MATERIAL

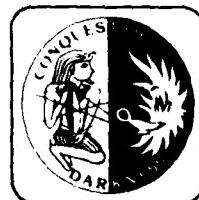
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Carol K. Pearce

April 1981

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) DELNV-TR-0020	2. GOVT ACCESSION NO. AD-A102 592	3. RECIPIENT'S CATALOG NUMBER
6. TITLE (and Subtitle) SPECTRAL SENSITIZATION OF DICHROMATED GELATIN (DCG) FOR AN IMPROVED HOLOGRAPHIC MATERIAL		5. TYPE OF REPORT & PERIOD COVERED Technical Report June 1979 December 1979
7. AUTHOR(s) (15) Carol K. Pearce	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS USAERADCOM: Night Vision and Electro-Optics Laboratory, Laser Division; Fort Belvoir, Virginia 22060	8. CONTRACT OR GRANT NUMBER(s)	
11. CONTROLLING OFFICE NAME AND ADDRESS (12) 28	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 16 1L161102A31B J0 64402A 17 J	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE April 1981	
	13. NUMBER OF PAGES	
16. DISTRIBUTION STATEMENT (of this Report)	15. SECURITY CLASS. (of this report)	
Approved for public release; distribution unlimited.	Unclassified	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Holography Lasers Dichromated gelatin Dyes Spectral sensitizers	Triplet sensitizers Phase holograms	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The report reviews use of dichromated gelatin in laser holograms and discusses some of the relevant background of dichromated gelatin technology. Spectral sensitization of this system would remove a major hindrance to its use for laser holograms. Suggestions are made for spectral sensitizer studies.		

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PREFACE

The contribution of Professor George R. Bird, Department of Chemistry, Rutgers University is acknowledged. Professor Bird has been enlightening and inspiring both in lectures and in informal discussions on dyes and photoimaging.

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CONTENTS

Section	Title	Page
	PREFACE	iii
	TABLES	v
I	INTRODUCTION	1
II	FUNDAMENTALS OF THE DICHROMATED GELATIN PROCESS	2
III	PROGRESS IN THE UTILIZATION OF DICHROMATED GELATIN FOR LASER HOLOGRAMS	6
IV	CANDIDATE SPECTRAL SENSITIZERS FOR DCG HOLOGRAPHIC TECHNOLOGY	10
V	CONCLUSIONS	15

TABLES

Table	Title	Page
1	Dye Sensitizers for Dichromated Gelatins	4
2	Possible Low-Energy Photosensitizers (Triplet)	12
3	Candidate Low-Energy Triplet Spectral Sensitizing for DCG	17
4	Suggested Laser DCG Dye Sensitizer Combinations	18

SPECTRAL SENSITIZATION OF DICHROMATED GELATIN (DCG)

FOR AN IMPROVED HOLOGRAPHIC MATERIAL

I. INTRODUCTION

Optical holography and the immense potential it presents for image storage and retrieval became a realistic challenge in 1962, when coherent laser light was achieved.¹ ² Three-dimensional imaging is one obvious achievement, since both the phase and amplitude information of a light wave can be recorded with holographic techniques. Conventional photography cannot do this, for it records amplitude only. A hologram can provide a three-dimensional recording of light scattered from an object. Reconstruction of the three-dimensional image of the object is accomplished by illumination of the hologram, using the same light frequency that was used to generate the hologram. Volume holography utilizes the thickness of the recording medium to store information.

Holograms, as Gabor described the recording of the interference fringes of (monochromatic) incident and reference waves of electromagnetic radiation, present modern technology with exploratory capacities for high-density data storage, coding and retrieval systems, for optical data processing systems, and for optical elements (lenses, gratings).³ Spectacular applications in holographic microscopy, or high-resolution volume imagery, have resulted in measurement of the size of objects as small as aerosol particles. Among the foremost applications of holography to Army needs must be the non-destructive testing of components. Precise information can be obtained about the extent and rates of vibration and deformation induced when external stress is applied, for example. Turning to the hologram itself, one finds that phase holograms can be produced that are excellent, replicable diffraction gratings. Applications involving memory systems may require the capability inherent in a volume hologram to store tremendous amounts of information (about 10^9 bits/mm²).⁴ Novel contributions have been made by holography to mapping and rangefinding with coherent radar particularly.⁵ Laser radar may extend the use of holography in these areas. A holographic lightline sight has been investigated.⁶ Visual orientation has been proposed with holograms serving as correlation filters and as guidance for blind aircraft landing.⁷

¹ M. V. Klein, "Optics," John Wiley & Sons, Inc., New York, 1970, pp. 392-407.

² D. Gabor, "Laser Devices & Applications," eds. I. P. Kaminow and A. E. Siegman, IEEE Press, New York, 1973, pp 450-463.

³ Ibid.

⁴ F. Bestenreiner, U. Greis, and W. Weiershausen, Photogr. Sci. and Eng., 16, 4 (1972).

⁵ W. E. Kock, "Engineering Applications of Lasers and Holography," Plenum Press, New York, NY, 1975, Chap. 9.

⁶ J. Upatnieks, "Investigation of Holographic Light-Line Sight," AD-B020191, Defense Documentation Center, Alexandria, VA April 1977.

⁷ N. Jewtchijew and D. Mirowicki, "Prospects for Holography," AD-A049389, Defense Documentation Center, Alexandria, VA September 1977.

Other applications are connected with semi-active homing and its use in seekers and trackers. Holograms of the terrain might be used similarly in maneuvering tanks and other military vehicles under poor visibility conditions. Furthermore, use of holographic methods for laser beam management and for goggles has been demonstrated recently.

Immense as the potential for holographic imaging is, however, a real-world limitation is imposed by the available recording media. For phase holograms, where modulation is achieved by a change in dielectric constant or in the thickness diffraction efficiencies can approach 100% theoretically, but with the commonly used Kodak 649F plate, efficiencies of only 60% to 70% are attained usually. When dichromated gelatin (DCG) plates are used, the efficiency can reach 90%.⁸ ⁹ Though the dichromated gelatin process may present long-term advantages as a non-silver consuming system, it is restricted by the light absorption of gelatin-dichromate to the blue spectral region and requires more intense exposures than the silver emulsion.¹⁰

Sporadic successes using dyes to sensitize dichromated colloids to the longer wavelengths of visible light have been reported, but spectral sensitization of dichromated gelatin as a holographic technique was not reported until 1973 (and published in 1974).¹¹ ¹²

II. FUNDAMENTALS OF THE DICHROMATED GELATIN PROCESS

Kosar has reviewed in detail the photographic technology of colloids (including gelatin) photosensitized with dichromate.¹³ Despite the problem of low light sensitivity and short shelf life, dichromated colloids are widely used today in applications of photographic resists and in photolithography. Basic to all such uses of dichromated gelatin is the cross-linking of molecular chains by chromic ion (Cr^{+3}), so that the gelatin which is water soluble when uncross-linked, becomes virtually insoluble. For use in photographic technologies, the gelatin is photosensitized with dichromate, which is reduced to Cr^{+3} upon irradiation with light. The desired cross-linking is initiated by the photo-generated Cr^{+3} . When the "hardening" is complete, the unhardened or uncross-linked areas remaining are simply washed off and the photographic image is produced on the plate.

⁸ J. W. Goodman, "Laser Devices & Applications," eds. I. P. Kaminow and A. E. Siegman, IEEE Press, New York, 1973, pp 450-463.

⁹ M. Lehman, "Holography," The Focal Press, New York, 1970, pp 105-132 esp.

¹⁰ M. Lehman, op cit.

¹¹ J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965, Chap. 2.

¹² M. Akagi, Photogr. Sci. Eng. 18 (3) 248 (1974).

¹³ J. Kosar, op cit.

Factors affecting the response of the dichromated gelatin layer include pH, dichromate concentration, coating thickness, and the emission spectrum of the light source used. Shelf life of the layer is affected by the thermal (or dark) reaction in which chromic acid is formed and is reduced, causing the colloid to be oxidized. Moisture, pH below 7, and temperature all contribute to formation of chromic acid and its deleterious effect on the gelatin layer. Sensitivity increases approximately as the dichromate concentration is increased, the limiting concentration being that at which dichromate crystallization appears. Adjustment of the pH of the dichromate sensitizing solution to values above 7 results in increased shelf life, since the dichromate-chromate equilibrium is shifted towards the chromate ion. The extent of hardening or gelatin cross-linking due to the dark reaction is reduced due to the lowered dichromate concentration. Optimum sensitivity occurs roughly in the pH range of 5 to 7, so use of higher pH values involves a trade-off of sensitivity for shelf life. Higher temperatures increase the rate of the dark reaction and result in shortened storage life. Moisture is necessary to the reaction by which dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, is reduced to Cr^{+3} . Some moisture is present in the coating even after the drying step of the preparation process. Gelatin absorbs moisture from the ambient and sensitivity increases with the moisture content but, unfortunately, the rate of the dark reaction does also. The thickness of the coating can be varied, thicker coatings requiring longer exposure times, but also affecting increased shelf life.

Finally, and perhaps most pertinent to this report, is the spectral distribution of the light source used. Maximum sensitivity for dichromated gelatin layers occurs in the UV, below 210 nm. The sensitivity falls off to a minimum around 320 nm. Another maximum, much lower than that below 210 nm, peaks around 360 nm and corresponds to the dichromate absorption. Sensitivity declines rapidly beyond this point, becoming non-existent around 580 nm.¹⁴ Thus for layers containing only dichromated gelatin, the most effective light source (excluding specialized sources peaking below 250 nm) will be those in which the 360 nm emission is dominant.

Sensitivity can be increased by modification of the gelatin-dichromate solution used to prepare the coatings. While alkali or ammonium dichromates are commonly used, pyridine dichromate can be substituted. Exposure times have been reduced by 1/3 with this substitution. The pyridine dichromate is less soluble in water, however, and also decomposes into pyridine and dichromic acid. The acid enhances the rate of the dark reaction, reducing the storage lifetime of the coated layer.

Spectral sensitization of DCG using dye sensitizers was reviewed by Kosar.¹⁵ Table 1 summarizes the dyes used. The research of Oster and Oster on

¹⁴ T. A. Shankoff, *Appl. Optics* 7 (10) 2101 (1968).

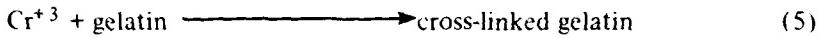
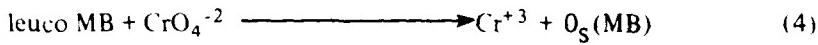
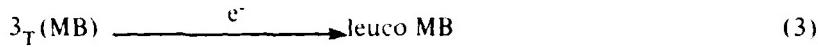
¹⁵ J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965, Chap. 2.

Table I. Dye Sensitizers for Dichromated Gelatin*

Dye	Other Additives	Spectral Range Sensitized	Investigator
Malachite Green	Moisture	orange-red	G. O.'t Hooft
Ethyl Cyanine	"	"	"
Pinatype Green D	"	"	"
Ethyl Violet	"	"	"
Erthrosine	"	"	"
Rose Bengal	"	"	"
Turquoise Blue	Absorption on AgI		Seymour
Methylene Blue		red	Jacobson & Wagner
Methylene Blue	EDTA	entire visible	Oster & Oster
Rose Bengal	Triethanolamine	"	Kerutsike, et al.
Rhodamine B	"	"	"
Eosin	"	"	"
Erythrosin	"	"	"

* J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965 Chap. 2.

dye-photosensitized cross-linking of DCG followed extensive studies on photo reductions of dyes, dye sensitized photopolymerization, and dye sensitized photo-reductions of metal ions (as CrO_4^{-2}).¹⁶⁻²³ The photosensitized cross-linking of DCG was attributed to the reductions of CrO_4^{-2} to Cr^{+3} by a dye (as methylene blue) in its reduced (leuco) form. The reduction of the dye resulted from the interaction of the photo-excited dye, in its lowest triplet state, with electron donors (as certain chelating agents) which reduce the excited dye but not the metal ion present. The mechanism may be represented, where MB represents methylene blue and * signifies an excited state as:



Chemicals can induce hardening (or insolubilization) of the gelatin in the absence of Cr^{+3} . Heat and actinic (UV) light are effective also. The type of hardening is not the same as that for DCG layers though. The precise mechanism for the DCG process resulting in gelatin cross-linking is still unknown.^{24 25}

¹⁶ G. K. Oster and G. Oster, J.A.C.S. 81, 5543 (1959).

¹⁷ G. K. Oster and G. Oster, J. Polymer Sci. 48, 321 (1960).

¹⁸ G. Oster, Phot. Eng. 4 (3), 173 (1953).

¹⁹ A. H. Adelman and G. Oster, J.A.C.S. 78, 3977 (1956).

²⁰ G. Oster and A. H. Adelman, J.A.C.S. 78, 913 (1956).

²¹ F. Millich and G. Oster, J.A.C.S. 81, 1357 (1957).

²² G. Oster and N. Witherspoon, J.A.C.S. 79, 4836 (1957).

²³ G. K. Oster, G. Oster, and G. Prati, J.A.C.S. 79, 595 (1957).

²⁴ J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965, Chap. 2.

²⁵ S. Suzuki, K. Matsumoto, K. Harada, and E. Tsubura, Photogr. Sci. & Eng. 12 (1) 2 (1968).

In contrast to the wealth of material available on the sensitivity of gelatin/silver halide emulsions, Kosar noted the relative absence of sensitometric evaluation of DCG. For the silver emulsions, H & D (Hurter and Driffield) curves relate the optical density (or amount of silver reduced) to the exposure E, or $\log E$, given the emulsion. Similar curves can be obtained for a DCG layer by exposing the layer through a photographic step wedge. The thickness of the hardened layer varies according to the depth of exposure to light. When the hardened layer is dyed and optical density (absorbance) measurements made, the thickness is related to the optical density and H & D curves characteristic of DCG may be made. Comparison of the characteristic (H & D) curves for DCG coatings with those for silver halide emulsions revealed that the optical density-log exposure relationship is linear over a longer range for the dichromate coatings than for the silver emulsions. Thus the dichromated gelatin produces an image that corresponds more accurately to the object. The slope of the linear portion, the gamma (γ), can be used as a comparative measure of the effects of variation in illumination sources, exposure times, and sensitizers.

Characteristic curves for DCG are *completely linear* when monochromatic illumination is used.²⁶ Such a linear "curve" portends the excellent results found when laser holograms are made using this material, results unknown at the time of Kosar's review.

III. PROGRESS IN THE UTILIZATION OF DICHROMATED GELATIN FOR LASER HOLOGRAMS

The need for high efficiency three-dimensional holographic gratings spurred investigations on DCG layers. Shankoff and Curran explored unhardened coatings sensitized with either $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ or pyridine-dichromate complex.²⁷⁻²⁹ Pre-hardened films prepared from gelatin with added glyoxal were used also, the dried film being sensitized by dipping in 4% aqueous $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Coatings were obtained with speeds up to two orders of that achieved with the (Kodak) 649F film commonly used for holograms. Best results were obtained when the plate was developed for 30 seconds in a 35°C water bath, followed by 30 seconds in isopropanol, and dried with a dry-air jet. Acetone, ethanol, butanol or glycol ethers could be substituted for isopropanol, but the organic solvent processing step was found to be essential for the desired surface etch. Holographic gratings were recorded usually with 488-nm argon laser radiation, unmodulated, using exposures of 3 to 8 mJ cm^{-2} (and up to 150 mJ cm^{-2}). The reduced spectral response of DCG at 488 nm compared to that at 380 nm was recognized. "Reading" of the holograms was done with 488-nm or

²⁶ J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965, Chap. 2.

²⁷ T. A. Shankoff, Appl. Optics 7 (10) 2101 (1968).

²⁸ T. A. Shankoff and R. K. Curran, Appl. Phys. Lett. 13 (7) 239 (1968).

²⁹ R. K. Curran and T. A. Shankoff, Appl. Optics 9 (7) 1651 (1970).

632.8-nm laser radiation. Extensive experimental and theoretical analyses supported the conclusion that DCG afforded highly efficient holographic gratings. Plane (linear), blazed, and Bragg-Lippman reflection phase gratings were made, as well as Fresnel zone plates.

Both were two- and three-dimensional phase gratings satisfied the Kogelnik criteria for sinusoidal phase gratings.³⁰ The two-dimensional gratings were thin holograms obtained with 0.5μ DCG layers, and the three-dimensional ones were thick coatings (up to 3.0μ). Relationships for thickness and diffracted power as a function of the exposure were given.³¹ The diffracted power peaked at 30%, corresponding to an exposure of 16 millijoules/cm², for the two-dimensional case. A leveling off of the diffracted power at about 80% occurred with the three-dimensional (1.3μ thick) grating upon exposure to 3 millijoules/cm² and higher. Exposures required for various thicknesses rose sharply from 20 millijoules/cm² for about 0.5μ to 90 millijoules/cm² for about 0.9μ , followed by a slower increase to about 145 millijoules/cm² for 2.2μ . The thick gratings gave a diffraction efficiency of 95% of the theoretical light output diffracted into the first order. The minimum grating space used was 0.26μ , and gratings of about 51,000 lines/inch were made. The gratings exhibited high optical quality, were ghost free, and gave background scatter of less than 10^{-4} of the signal. Photomicrographs revealed a layered or onionskin-like structure of the grating.³² Replication of the gratings with Plexiglas were successful. The experimental results are consistent with the model of a surface grating caused by the difference in refractive index at an air-gelatin interface. A mechanism for the formation of the highly efficient diffraction grating hologram was advanced, wherein the critical air-gelatin interface was created by cracks formed when the isopropanol development step rapidly dehydrates the swollen coating. Reciprocity law failure was found. The exposure energy required to achieve a given diffraction efficiency was found to vary in an oscillating manner with thickness, rather than inversely.³³

Another technique for making DCG holograms was investigated by Lin.³⁴ Hardened gelatin films were prepared by processing an undeveloped Kodak 649F emulsion through a fixing bath and then through water and methanol washes. The gelatin film remaining is sensitized by immersion in 5% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ solution. After exposures of up to 50 mJ/cm² of 488-nm argon laser emission, the film is developed

³⁰ T. A. Shankoff, *Appl. Optics* 7 (10) 2101 (1968).

³¹ *Ibid.*

³² R. K. Curran and T. A. Shankoff, *Appl. Optics* 9 (7) 1651 (1970).

³³ *Ibid.*

³⁴ L. H. Lin, *Appl. Optics* 8 (5) 963 (1969).

(after a reduction step) with a 5-minute water wash (20°C), then 2 minutes in isopropanol, and then air dried. To assure a clear hologram and low noise reconstruction, a reduction step is required: 5 minutes in 0.5% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and 5 minutes in a reducing agent (as 2% sodium bisulfite (sic) solution or Kodak Rapid Fixer).

Both transmission and reflection holograms were made and a "large" linear recording range found for plots of the square root of diffraction efficiency versus exposure.³⁵ This means that in the linear recording range the amplitude of the reconstruction wavefront corresponds linearly to the amplitude to the wavefront to which the hologram was originally exposed. A maximum diffraction efficiency of almost 90% was obtained. Finally, the holograms exhibited little "noise," or light scattering, and afforded relatively permanent volume recordings. (The clear hologram produced in DCG signifies low noise and is most desirable. No dyeing is required, as is done sometimes in other DCG uses.) Water or high humidity affected the holograms. These are multiple-use films and could be resensitized so that additional recordings could be made. Only the slow speed and its restricted spectral response detracted from the excellent holographic performance of DCG.

The potential for replication exhibited by DCG relief phase holograms caused Meyerhofer to examine the spatial resolution in such holograms.³⁶ Using unhardened (ammonium) dichromated gelatin, he found that development with a simple water wash gave good diffraction efficiency and very low scattering. Higher diffraction and modulation efficiencies, but more scatter or noise, was produced when the isopropanol wash step was added to the development process. The noise was believed due to the "ridges" or cracks typical of this development method. The cracks would make good replication difficult also. Detailed studies were made of the modulation of the DCG thickness (corresponding to the recording on the hologram), and at grating spacings of below a few microns, the modulation began to decrease and became less efficient in films given only a water development. Exposures were accomplished with collimated 441-nm He-Cd laser radiation having a beam flux of 10 mW cm^{-2} .

To offset the slow speed and limited spectral response of DCG, a novel but complex process was investigated by Pennington, Harper, and Laming.³⁷ Recordings on conventional silver halide emulsions are bleached to attain low-noise, high-efficiency holograms. These silver images darken when exposed to blue or UV light, so that reconstruction of the hologram becomes unsatisfactory. DCG holograms do not darken, however, the process detailed by these authors affords phase holograms with

³⁵ I. H. Lin, *Appl. Optics* **8** (5) 963 (1969).

³⁶ D. Meyerhofer, *Appl. Optics* **10** (2) 416 (1971).

³⁷ K. S. Pennington, J. S. Harper, and L. P. Laming, *Appl. Phys. Lett.* **18** (3), 80 (1971).

the high diffraction efficiencies (over 60%) of DCG and signal-to-noise ratios of 70:1. Further, photographic speeds are much faster (orders of magnitude of 10^2 to 10^5) than for DCG, and the spectral response is panchromatic. The process has been used for multicolor recordings. Basically, the process utilizes the recording of a hologram on a silver halide emulsion, developing it and then bleaching it. The bleached hologram is dipped in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ solution, and then exposed to 488 nm argon laser radiation. Excess dichromate is removed by washing in bisulfite solution, silver compounds are removed by fixing solution, and then developed as DCG with hot water and isopropanol washes.

Use of hardened DCG for phase holograms was investigated by Kawatani and Watanabe, confirming the high diffraction efficiency of such holograms.³⁸ Hill and Watanabe constructed a thin-film optical waveguide from a DCG holographic phase grating and an optical flat. This was filled with a Rhodamine 6G solution, resulting in a (N_2 laser pumped) dye laser with distributed feedback.³⁹

Spectral sensitization of DCG was investigated by Akagi for recording holograms with 633-nm He-Ne laser emission.⁴⁰ Based upon Oster and Oster's work on dye-sensitized DCG, the procedure involved incorporating methylene blue in the $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ -gelatin sensitizing solution.⁴¹⁻⁴² Several acid amides (acetamide; N,N-dimethylformamide; N-methyl-2-pyrrolidone) were found to give better results than the EDTA used by Oster as a reducing agent. A hot water wash development was used. Both grating and pictorial images were recorded as holograms.

DCG has been most useful for phase holograms in the reports reviewed above. Despite the lack of sensitometric data Kosar noted in DCG work, most of the DCG holographic work contained measurements of a holographic property (usually diffraction efficiency) as a function of exposure. One can expect that as the DCG holographic technology is explored further and refined, criteria suggested for silver halide emulsions in holography will be applied to DCG.⁴³⁻⁴⁵ Amplitude transmittance as well as holographic efficiency, both as a function of exposure, should become basic criteria. Spectral sensitivity curves will be required especially in efforts to extend the spectral response range of DCG. While a novel process has been proposed which

³⁸ T. Kawatani and T. Watanabe, Denk. Tsushin Kenkyojo Kenkyu Jitsuyoka Hokoku 20 (1) 271 (1971), reported as Chemical Abstract 75, #103634n.

³⁹ K. O. Hill and A. Watanabe, Opt. Commun. 5, 389 (1972), as reported by T. W. Hansch, "Dye Lasers," ed. F. P. Schaefer, Springer-Verlag, Berlin-Heidelberg, 1973, p. 251.

⁴⁰ M. Akagi, Photogr. Sci. Eng. 18(3) 248 (1974).

⁴¹ G. K. Oster and G. Oster, J.A.C.S. 81, 5543 (1959).

⁴² G. K. Oster and G. Oster, J. Polymer Sci. 48, 321 (1960).

⁴³ D. G. Falconer, Photogr. Sci. & Eng. 10 (3) 133 (1966).

⁴⁴ H. Nassenstein, H. Dedden, H. J. Metz, H. E. Rieck, and D. Schultze, Photogr. Sci. & Eng. 13 (4) 194 (1969).

⁴⁵ M. DeBelder, Photogr. Sci. & Eng. 13 (6) 351 (1969).

combines the best features of both silver halide emulsions and DCG, it is a lengthy and complex procedure. The simplicity of a dye-sensitized DCG process suggests the spectral sensitization of DCG may be an important area of research. From the review above, in fact, it is the most neglected area in DCG holography. Success in this area would remove a major difficulty with DCG.

IV. CANDIDATE SPECTRAL SENSITIZERS FOR DCG HOLOGRAPHIC TECHNOLOGY

The probability that holograms will need to be recorded across all of the visible spectrum, at least, becomes an increasing reality with the continuing development of laser technology. Already dye laser emission is tunable from about 400 to 1000 nm, and various semiconductor lasers operate over this range as well. Neodymium⁺³ (1.06 μ), holmium⁺³ (2.1 μ), and erbium⁺³ (1.54 μ) in glass or crystalline hosts are in use. Ruby (694 nm), helium-neon (633 nm), argon ion (514.5 nm), helium-cadmium (441 nm), and nitrogen (337 nm) are common. Yet only one dye, methylene blue, has been used as a spectral sensitizer for DCG holograms. Little more has been done on the spectral sensitization of DCG itself. Comparison of the appropriate sensitometry of DCG holograms produced with different dyes as sensitizers, should extend the useful DCG range over the visible spectrum.

Guidance in directing the choice of candidate sensitizers comes initially from the dyes reviewed in Table 1 and from photochemical studies with triplet sensitizers. Extensive studies on spectral sensitization of silver halide emulsions have been done, but the basic mechanism is still elusive.⁴⁶ Both electron transfer and energy transfer mechanisms have been advanced for the silver films, but not even that much has been achieved for DCG.⁴⁷ The mechanism operating in DCG may be quite different from that in the silver system. The effect of the crystalline character present in silver halide films has been cited in studies of dye-sensitized emulsions.^{48 49 50} DCG layers always contain some water, as evidenced by the dark reaction problem,⁵¹ so that at least as a first approximation — the system could be considered a liquid or non-ordered one.

⁴⁶ W. West, Photogr. Sci. & Eng. 18 (1) 35 (1974).

⁴⁷ S. Suzuki, K. Matsumoto, K. Harada, and E. Tsubura, Photogr. Sci. & Eng. 12 (1) 2 (1968).

⁴⁸ W. D. Pandolfe and G. R. Bird, Photogr. Sci. & Eng. 18 (3) 340 (1974).

⁴⁹ D. Mastropaoletti, J. Potenza, and G. R. Bird, Photogr. Sci. & Eng. 18 (4) 451 (1974).

⁵⁰ G. R. Bird, Photogr. Sci. & Eng. 18 (5) 562 (1974).

⁵¹ J. Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York, 1965, Chap. 2.

Oster and Oster's findings were reviewed above. More recent studies support their conclusions. Tanaka et al. photoreduced methylene blue in the presence of α -dimethylphenyl glycine (DMPG).⁵² The solutions were deoxygenated to control oxidation of reduced (leuco) MB. Oster's (et al.) work on MB solutions also was done on deaerated samples.^{53 54} Tanaka noted that other derivatives of N-Phenyl-glycine or N-phenylalanine could serve as reducing agents though DMPG gave a higher quantum yield. Pulsed ruby laser irradiation was used, with output energy of 150 mJ. The lowest triplet absorption was given as around 7000A° , which corresponds to about 40 kcal mol^{-1} .

These results suggest that initially the useful criteria for spectral sensitizer candidates (DCG) would be:

- a. A triplet level about 40 kcal mol^{-1} .
- b. Absorption maximum in the visible.
- c. Water solubility to give a solution of about 10^{-4} M at least.
- d. High quantum yields, Φ , for triplet formation.

This can be deduced from Φ_{ST} (for intersystem crossing) or from Φ_p/Φ_f , the ratio of quantum yields for phosphorescence and fluorescence.⁵⁵ Phosphorescence is associated with decay from a triplet and fluorescence from a singlet to the ground state. Low separation between the $^1\text{S}^*$ and the lowest sensitizer triplet would also contribute to a higher triplet population. Compilations of some of these values from the photochemical literature have been made. Table 2 presents values for compounds with triplet (lowest) levels below about 57 kcal mol^{-1} . The limit was picked somewhat arbitrarily since it corresponds to the "low-energy" range of triplet sensitizers found by Hammond (et al.) for cis-trans isomerizations.^{56 57} Further, since the first triplet level would be lower than the first excited singlet, and absorption in the visible is desired, the singlet would be above 500 nm ($=2.85 \times 10^5/57$). Because of the low dye concentration used by Oster et al., no information is included on water solubility, but the pure hydrocarbons (nonpolar) may be eliminated by this criterion. More triplets might be obtained with an extended literature search. The present search yielded some Φ_{ST} values but no Φ_p or Φ_f on the same compounds.

⁵² I. Tanaka, Y. Mori, Y. Minagawa, and E. Okutsu, J. Phys. Chem. 72 (7) 2684 (1968).

⁵³ G. K. Oster and G. Oster, J.A.C.S. 81, 5543 (1959).

⁵⁴ G. Oster and N. Witherspoon, J.A.C.S. 79, 4836 (1957).

⁵⁵ N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967, Chap. 5.

⁵⁶ G. S. Hammond and J. Saltiel, J.A.C.S. 84 4983 (1962).

⁵⁷ G. S. Hammond et al., J.A.C.S. 86 3197 (1964).

Table 2. Possible Low-Energy Photosensitizers (Triplet)

Symbols: E_T = Triplet Energy; Φ_{ST} = Intersystem Crossing Yield; E_S = First Singlet Level; $\lambda_{max,abs}$ = wavelength of maximum absorption

Compounds	E_T , kcal/mol	Φ_{ST}	E_S , kcal/mol	$\lambda_{max,abs}$, nm*†
Acridine Yellow ^a	58.0			
Diphenyldiacetylene ^b	58.0			
1-Naphthoic Acid ^b	57.5			293
1-Naphthonitrile ^b	57.5		89.1	
1-Benzoylnaphthalene ^b	57.5			
2,3-Benzofluorene ^b	57.4			
1,2-Benzofluorene ^b	57.4		83.3	
Chrysene ^b	57.3	0.85		220-360
2,3-Butanedione ^b	57.2			
1-Naphthylphenylketone ^a	57.0			
3,4,5,6-Dibenzophenanthrene ^b	56.6		72.3	
1-Acetyl naphthalene ^b	56.5			
5,6-Benzochrysene ^b	56.5		74.1	
1-Naphthaldehyde ^b	56.4			
1-Acetonaphthone ^a	56.0			
2,2'-Binaphthyl ^b	55.8			
Diphenyltriacetylene ^b	55.4			
3,4-Benzofluorene ^b	55.3			
Biacetyl ^a	55.0			
1-Nitronaphthalene ^b	54.9			
Coronene ^b	54.4	0.56		
Benzil ^b	54.3			
1-Aminonaphthalene ^b	54.3			
Diethyltetraacetylene ^b	53.8		80.7	
Tetraacetylene glycol ^b	53.7		81.0	
1,2-Benzochrysene ^b	53.3		77.1	
Fluorenone ^{a, b}	53.0	0.93		
Fluoranthene ^b	52.9		79.8	
1,2-Benzopyrene ^b	52.9		78.1	
1,2,7,8-Dibenzanthracene ^b	52.9			
1,2,5,6-Dibenzanthracene ^b	52.2		72.6	
1,2,3,4-Dibenzanthracene ^b	50.8		76.3	283-375
Fluorescein ^c	50.0			493.5(Na Salt)
Fluoresceine (acid) ^a	51.0			270-380
trans-4-Nitrostilbene ^a	50.0			

Table 2. Possible Low-Energy Photosensitizers (Triplet) (Cont'd)

Compounds	E_T , kcal/mol	Φ_{ST}	E_S , kcal/mol	$\lambda_{max,abs}^*$, nm*†
Diphenyltetraacetylene ^b	49.0		66.7	
Pentaphene ^b	48.4		67.5	220-390
Pyrene ^a	48.2	0.27;0.88	67.5	255-319
Acridine orange ^c	48.0			
9,10-Benzanthrone ^d	48.0	c.1		290-420
1,2-Benzanthracene ^b	47.2	0.82		285-385
Eosin Y ^c	47.0			519
trans-1,3,5-Hexatriene ^b	47.0			
Benzanthrone ^c	47.0			
3-Acetylpyrene ^c	45.5			
11,12-Trimethylenetetraphene ^a	46.0			
1,12-Benzperylene ^b	46.2			
Phenazine ^a	44.0			260-340
Eosin ^a	43.0			
Acridine ^c	45.3			340-260
Anthracene ^b	42.7	0.70;0.72		247-375
9,10-Dimethyl-1,2-benzanthracene ^c	44.3			
3-Acetylpyrene ^a	43.0			
Sulforhodamin B ^c	45.0			
1-Chloroanthracene ^b	42.1			
Erythrosin B ^c	45.0			528
Rose Bengal ^c	43.0			550
3,4-Benzopyrene ^b	42.0		70.8	257-400
9,10-Dibromoanthracene ^a	40.0			258-585
9,10-Dichloroanthracene ^b	40.4			
Thiobenzophenone ^a	40.0			
Crystal violet ^a	39.0			586
Hematoporphyrin ^c	37.0			615,565,534,499
Perylene ^b	35.1	0.0088	65.8	250-435
Methylene Blue ^c	33.0			668,609
Naphthacene ^a	29.0			393-471

Table 2. Possible Low-Energy Photosensitizers (Triplet) (Cont'd)

Compounds	E_T , kcal/mol	Φ_{ST}	E_S , kcal/mol	$\lambda_{max,abs}^*$, nm†
Chlorin e ₆ ^c	35.0			
Tetracene ^b	29.3			393-471

* "The Merck Index," 8th ed., Merck & Co., Rahway, NJ, 1968.

† O. W. Wheeler and L. A. Kaplan, eds., "Organic Electronic Spectral Data," vol. III, Interscience, New York, 1966.

^a N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967, Chap. 5.

^b S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, Inc., New York, 1973, Sections 1-4.

^c D. R. Kearns et al., J.A.C.S. 89 (21) 5455 (1967).

^d T. A. Shankoff and A. M. Trozzolo, Photogr. Sci. & Eng. 19 (3) 173 (1975).

^e W. G. Horkstroeter and G. S. Hammond, J.A.C.S. 88 (21) 4769 (1966).

Absorption maxima should not be too difficult to obtain either experimentally on pure compounds or from the literature. The triplet quantum yields appear to be a real gap in Table 2.

Oster et al., found further that dye photoreduction is the rate-determining step for dye-sensitized photoreduction of metal ions. The only effective dye sensitizers were those capable of photoreduction. Of the various families of dyes, all of the thiazines (MB, azure A, etc.) and fluoresceins (fluorescein; its halogenated derivatives as eosin, erythrosin, etc.) and also the 3,6-diaminoacridines were photoreducible. The authors noted that none of the azo or azine dyes were effective.

Early in his studies on photoreduction, Oster noted the "diversity of photoreducible systems," and warned that, "In each system there are delicate reduction potential conditions which must be satisfied in order for the photochemical reaction to proceed."⁵⁸ Relating dye sensitization performance to electrochemically determined oxidation and reduction potentials and to ionization energy and electron affinity, and in turn relating such parameters to the energy levels present in the dyes is an on-going process. An incomplete referencing is included.^{59 60 61 62 63 64}

⁵⁸ G. Oster, Phot. Eng. 4 (3), 173 (1953).

⁵⁹ J. W. Trusty and R. C. Nelson, Photogr. Sci. & Eng. 16, 421 (1972).

⁶⁰ R. C. Nelson and R. G. Selsby, Photogr. Sci. & Eng. 14, 342 (1970).

⁶¹ T. Tani, Photogr. Sci. & Eng. 14, 237 (1970).

⁶² P. Nielsen, Photogr. Sci. & Eng. 18 186 (1974).

⁶³ I. H. Leubner, Photogr. Sci. & Eng. 18 175 (1974).

⁶⁴ I. H. Leubner, Photogr. Sci. & Eng. 20, 61 (1976).

These studies consider the dye, its host (here, silver halide), and dye aggregation and attempt to make meaningful relationships for them. Eventually, similar relationships may be found for dye sensitizers *in situ* in DCG. Basic to these "electrochemical" concepts seems to be the assumption that excited state behavior parallels that determined in the ground state. The discussion following Leubner's presentation treats measurements of redox potentials of excited dyes, indicating that this assumption might not be successful.⁶⁵ Spectroelectrochemical techniques are available now which may be useful in clarifying the relationship between electrochemical potentials in ground and excited states of dyes.⁶⁶

V. CONCLUSIONS

Review of the use of DCG for laser holograms suggests that one of the chief deterrents to its more widespread use is its lack of spectral response beyond 580 nm and a rapidly decreasing sensitivity at wavelengths longer than 360-380 nm. Achievement of spectral sensitization across the visible for DCG will benefit holographic technology and contribute to the knowledge of spectral sensitizers.

Because so little work has been done on spectral sensitization of DCG, this problem as well as the application to laser holograms must be studied. A possible approach might be:

1. Initial choice of compounds may be made from Tables 1 and 2, using those with the lowest triplet levels (especially those in Table 2, $E_T \leq 50$), highest triplet yield, and smallest gap between the first excited singlet and the lowest triplet. Absorption spectra should show visible maxima corresponding to the laser used, or monochromatic source. Absorption spectra should be run of the DCG layers studied below, to discern any effect of the medium on the dye.

2. "Scanning" of the candidate sensitizers may be done by following the decay in dye absorption with laser exposure, using deoxygenated aqueous solutions of the dye, and each of the reducing agents in references 67, 68, 69, and 70.

⁶⁵ I. H. Leubner, Photogr. Sci. & Eng. 18 175 (1974).

⁶⁶ T. Kuwana and W. H. Heineman, Accts. Chem. Res. 9 (7), 241 (1976).

⁶⁷ M. Akagi, Photogr. Sci. Eng. 18 (3) 248 (1974).

⁶⁸ G. K. Oster and G. Oster, J.A.C.S. 81, 5543 (1959).

⁶⁹ G. K. Oster and G. Oster, J. Polymer Sci. 48, 321 (1960).

⁷⁰ I. Tanaka, Y. Mori, Y. Minagawa, and E. Okutsu, J. Phys. Chem. 72 (7) 2684 (1968).

3. Promising sensitizers may be incorporated in DCG layers. Deoxygenation appears not to be a problem here, for the regeneration of the dye would be useful for inducing further Cr^{+3} -cross-linking. Characteristic H & D (or thickness vs. log exposure) curves, noise (scatter), and diffraction efficiency (for gratings) vs. exposure are the minimal measurements that should be run.

4. Spectroelectrochemical measurements of spectral sensitizers should be considered, with the aid of relating known energy levels with excited state potentials. It may be possible to create a cell for these measurements close to the conditions found in dye-sensitized DCG.

More definitive choices of candidate compounds will be possible as more information on energy levels and absorption spectra (visible) is obtained. Table 3 gives some compounds which meet the criteria of visible light absorption, low energy triplet levels, and the probability of a high triplet quantum yield. One would expect these compounds to be the most efficient in effecting cross-linking in DCG assuming that they are photoreducible. The compounds (except hematoporphyrin and chlorin e₆, which are in the porphyrin class of compounds) are among those classified by Oster as photoreducible. Oster's studies utilized deaerated solutions as was suggested above for scanning candidate compounds. Since oxygen is a triplet quencher the photo-reduction experiments could be affected adversely. Oster did not deaerate his DCG layers, though. When quantitative studies are done on the dye-sensitized DCG, however, deaerating (perhaps by flushing the equilibrating with an inert gas as nitrogen, argon, helium) may be necessary for step (3) of the DCG mechanism and should be used for step (4) also.

The efficiency of DCG cross-linking in step (3) should be related to the dye-sensitizer and the laser used. If it is found that the cross-linking is sufficiently sensitive to the match between dye absorption and laser emission shown in Table 4, derivatives of the dye should be sought to "fine tune" the dye to the laser used. Tunable dye lasers would be useful for obtaining the optimum match. By maximizing the match of the dye and the laser for efficient spectrally sensitized cross-linking, exposure times for DCG should be minimized though the time for the cross-linking process would not be affected. Both spectral response and long exposure times have been cited as deficiencies in the use of DCG for laser holograms. The long exposure times may be due in part to inefficient utilization of the exposure light by DCG, so that optimizing dye-sensitization may reduce the effect of both deficiencies.

Successful dye sensitization of DCG as suggested above would greatly expand the range of volume and phase holography using this medium. One can anticipate that practical limits for memory storage will be expanded and that more accurate imaging will be obtained when visible light sensitivity is realized. Improved gratings, as well as microimaging, can be anticipated.

Table 3. Candidate Low-Energy Triplet Spectral Sensitizing for DCG

Symbols: E_T = Triplet Energy; E_S = First Singlet Level; $\lambda_{abs,max}$ = wavelength of maximum absorption

Compound	E_S kcal/mol ⁻¹	E_T kcal/mol ⁻¹	$E_S - E_T$, calc kcal/mol ⁻¹	$\lambda_{abs,max}$ nm*†
Fluorescein ^{a b}		50	4.5	493.5(Na Salt)
	54.5			
Acridine orange ^{a b}		48	7.0	496,467 ^c
	55.0			494 ^d
Eosin Y ^{a b}		47	3.6	519
	50.6			
Erythrosin B ^{a b}		45	4.5	528
	49.5			
Rose Bengal ^{a b}		43	6.3	550
	49.3			
Hematoporphyrin ^{a b}		37	8.0	615,565,534,499
	45.4			
Methylene Blue ^{a b}		33	8.4	668,609
	41.4			
Chlorin e ₆ (Phyto-chlorin) ^{a b}		35	7.7	
	42.7			

* "The Merck Index," 8th ed., Merck & Co., Rahway, NJ, 1968.

† O. W. Wheeler and L. A. Kaplan, eds., "Organic Electronic Spectral Data," vol. III, Interscience, New York, 1966.

^a D. R. Kearns et al., J.A.C.S. 89 (21) 5455 (1967).

^b Calculated from fluorescence maxima in: A. Nickon and W. L. Mendelson, J.A.C.S. 87 (17) 3921 (1965).

^c L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath & Co., Boston, 1944, p. 834.

^d F. Millich and G. Oster, J.A.C.S. 81, 1357 (1957).

Table 4. Suggested Laser and DCG Dye Sensitizer Combinations

Laser	Laser Wavelength (nanometers)	Sensitizer Dye	Wavelength Maximum for Dye Absorption (nanometers)
Ruby	694	Methylene Blue	668,609
Helium-Neon	633	Methylene Blue Hematoporphyrin	668,609 615,565,534.499
Argon ion	514.5	Eosin Y	519
		Erythrosin B	528
		Rose Bengal	550
		Acridine orange	496,467
		Fluorescein(Na Salt)	494
Helium-Cadmium	441	Fluorescein(Na Salt)	494
		Acridine orange	496,467

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- ⁴³ D. G. Falconer, Photogr. Sci. & Eng. 10 (3) 133 (1966).
⁴⁴ H. Nassenstein, H. Dedden, H. J. Metz, H. E. Rieck, and D. Schultze, Photogr. Sci. & Eng. 13 (4) 194 (1969).
⁴⁵ M. DeBelder, Photogr. Sci. & Eng. 13 (6) 351 (1969).

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